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Xenobiotics removal by membrane technology: an overview

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Abstract

Small molecular weight xenobiotics are compounds of extreme concern in potable water applications due to their adverse human health and environmental effects. However, conventional water treatment processes cannot fully and systematically remove them due to their low concentrations in natural waters and wastewaters. Biological limitation to degrade such compounds is another cause for inefficient removal.

Physical barriers like membranes possessing pore sizes smaller than the compounds to be removed emerged as a good solution. Nanofiltration and reverse osmosis proved to be quite effective for xenobiotics removal in potable water production in the Paris purification plant of Méry-sur-Oise. However, even these very narrow pore membrane processes may result in incomplete removal: xenobiotics retention is high but factors such as adsorption, size exclusion and charge repulsion affect unpredictably their retention. The water solutions complexity to be treated renders xenobiotics removal predictions even more difficult due to interactions between xenobiotics and compounds in water.

Removal of xenobiotics by microfiltration and ultrafiltration is very low because adsorption on the membrane is the main retention mechanism. Combining those with other processes (e.g. activated carbon) can considerably improve xenobiotics removal.

The least studied processes in xenobiotics removal are electrodialysis, membrane distillation and pervaporation. Electrodialysis removal of organic xenobiotics shows a breakthrough through the membrane possibly due to adsorption followed by diffusion. Membrane distillation presents high removal rates of xenobiotics due to the compounds low vapour pressure. For volatile organic xenobiotics or solutions of trace amounts both membrane distillation and pervaporation can be used, xenobiotics interaction with the membrane being the key factor.

In this book chapter a thorough synopsis of current knowledge on xenobiotics removal is presented and balanced with recent fundamental studies of underlying mechanisms, informing both the practitioner regarding membrane capabilities for xenobiotics removal and the researcher with the current state-of-art.

Keywords: membrane processes, xenobiotics, fouling, adsorption, charge repulsion, size exclusion

1 Introduction

1.1. Xenobiotics removal by conventional water treatment processes and natural water contamination

Xenobiotics are compounds foreign to a living organism or introduced in the environment by artificial means. The implications of xenobiotics on human health, including endocrine disruption, have been intensively debated recently [131, 149, 113]. Although studies are to date not conclusive, it is important to remove xenobiotics from wastewaters discharged to surface waters as well as protecting drinking water sources.

Concentrations of xenobiotics up to µg/L were measured in wastewater treatment plant (WWTP) effluents, showing an incomplete removal by conventional treatment processes all over the world [11, 68, 153, 57, 67, 142, 120]. Batt et al. [12] measured a total concentration of active pharmaceuticals up to 3,000 ng/L in New Mexico of which carbamazepine concentration was up to 800 ng/L. Carbamazepine and paracetamol were found at high concentrations, 300 ng/L and 11.3 mg/L respectively, in the Hérault area, France [108]. High concentrations of antidepressants in Minnesota, USA [120] and pharmaceuticals in the Berlin area, Germany [50] were also measured.

These effluents are discharged into surface and groundwaters where concentrations up to µg/L were measured for pharmaceuticals, anti-depressants and hormones [62, 12]. Rabiet et al. [108] showed that wells tapped for drinking water in the vicinity of WWTPs had concentrations of pharmaceuticals up to 300 ng/L compared to other wells with <50 ng/L upstream from the plant. The same phenomenon was found with surface waters downstream of a WWTP in the Berlin area [50]. In a UK survey on two rivers in the southeast of England an increase in estrone concentration was measured caused by a WWTP discharge [142]. Although hormones were measured at trace level concentrations in these effluents, in USA streams concentrations of more than 100 ng/L were quantified [67].

There are thousands of xenobiotics of concern most of which are small and occur at low concentrations making them very difficult to remove effectively. Due to an insufficient removal by conventional treatment processes, the application of advanced technologies such as membrane processes have been the focus of attention since they have the potential to efficiently remove xenobiotics down to very low levels.

1.2. Target xenobiotics

Six organic xenobiotics were chosen as example compounds for this chapter due to the extensive availability of data from different types of membrane filtration studies and due to their different physico-chemical properties. This choice allows the illustration of different behaviours of xenobiotics in different membrane processes. The chemical properties of the xenobiotics are described in Table 1. The pK_a and Log K_{ow} represent the acid dissociation constant and the partition coefficient in octanol-water, respectively. The latter is a measure of the compound hydrophobicity.

Sulfamethoxazole (SMX), estrone, bisphenol-A (BPA), fluoranthene and carbamazepine (CBZ) have approximately the same molecular weight (MW). They differ in their dipole moment, Log K_{ow} and pK_a. They are all bipolar, with the exception of fluoranthene, meaning they can act either as a proton (H) acceptor or donor, being able to form H-bonds with other molecules [45].

TABLE1

1.3. Membrane processes

Membranes work as a physical barrier to the passage of contaminants, with pores or molecular channels incorporated into a polymeric material. The most common membrane processes for water treatment applications are pressure driven. Exerting pressure perpendicular to the membrane (driving force) allows the passage of water through, the permeate, and the retention of

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solutes and contaminants, the concentrate, from a feed solution that circulates tangentially to the membrane surface (see equation (4) and Figure 1).

FIGURE1

Membranes are either porous, e.g. ultrafiltration (UF) and microfiltration (MF), or dense, e.g. reverse osmosis (RO). Nanofiltration (NF) membranes are considered to be between porous and dense [116]. These differences dictate how the contaminant is transported through the membrane. MF and UF membranes are characterised by the molecular weight cut-off (MWCO), an indication of the compounds size they remove, corresponding to the MW at which 90% rejection is obtained [84]. NF can be either characterised by MWCO or ionic retention of salts such as NaCl or $CaCl_2$. RO membranes being dense are characterised by salt rejection, although some researchers have modelled molecular retention to determine a MWCO [65].

Retention of a contaminant is defined as:

$$R_{xenobiotic}(\%) = 100 \times (1 - \frac{c_P}{c_F}) \quad \textbf{(1)}$$

Where c_P and c_F are the permeate and feed concentrations, respectively.

Other common performance parameters for membrane processes are:

$$Q_F = Q_C + Q_P \quad \textbf{(2)}$$

$$\text{Recovery} = \frac{Q_P}{Q_F} \quad \textbf{(3)}$$

$$J = \frac{1}{A}\frac{dV}{dt} = L_P(\Delta P - \Delta\pi) \quad \textbf{(4)}$$

Where Q_F, Q_C and Q_P are feed, concentrate and permeate flow rates, recovery is the amount of clean water produced per feed water treated, A is the membrane area, V is the permeate volume, t is time, L_P is the membrane permeability, ΔP is the applied transmembrane pressure and $\Delta\pi$ is the osmotic pressure difference between feed and permeate.

Several types of membrane processes are available for water treatment depending on their separation principle, pore size d_P (see Figure 1), and driving-force for separation. The different membrane processes found are pressure driven as described in Figure 1 (MF, UF, membrane bio-reactor MBR, NF and RO), electrical potential driven (electrodialysis ED), thermally driven (membrane distillation MD) and due to vapour pressure differences between feed and permeate (pervaporation PV). A comparison between different membrane separation processes described in this chapter and solutes they remove is presented in Table 2. The MW range of the compounds and membrane pore sizes or particle sizes are also presented.

TABLE2

Membrane separation processes are in principle able to remove from contaminants as big as bacteria (e.g. MF, UF, membrane bio-reactor, NF and RO) to small contaminants such as xenobiotics and metal ions (e.g. NF, RO and ED).

2 Microfiltration, ultrafiltration and membrane bioreactors

MF and UF processes use porous membranes that act as a sieve, with pore size ranging between 50-10,000 nm (MF) and 1-100 nm (UF) [84]. Separation of molecules takes place by steric hindrance at the inlet of the pore and by frictional resistance inside the pores [15]. UF membranes separate smaller contaminants than MF given their smaller pore size as can be seen in Table 2. A key advantage of UF over MF in water treatment is that UF removes bacteria and most viruses and is hence a physical disinfection process.

To separate small molecules such as xenobiotics it is necessary for these compounds to precipitate, adsorb or coagulate to a bigger size to allow for MF or UF retention. However

exceptions have been found where high apparent retentions are obtained although xenobiotics sizes are much smaller than membrane pore size, as described next.

A simplified schematic of the several mechanisms involved in xenobiotics retention by MF and UF membranes is shown in Figure 2.

FIGURE2

2.1. Xenobiotics removal by MF and UF

Due to the relatively large pore sizes of MF and UF membranes (see Table 2) xenobiotics generally of MW lower than 400 g/mol are not retained even by the lowest MWCO membranes [34, 146, 147]. However studies show the occurrence of adsorption by some of the membrane polymers [117] leading to apparent high retention.

Chang et al. [23] obtained 100% removal of estrone in a MF dead-end process due to adsorption on the membrane. A sieving effect is discarded since the membrane pores are much larger than the estrone molecule. This occurs due to low estrone feed concentrations, where the amount of adsorption sites available on the membrane allows for adsorption of almost all the contaminant. High adsorption of xenobiotics have also been obtained in several UF studies [148, 146, 29]. Fluoranthene and 17β-estradiol adsorbs onto UF membranes from >70% for fluoranthene and >34% for estradiol [148]. Although MF and UF have apparent high retentions for small xenobiotics they are related with adsorption on the membrane surface. Once adsorption sites saturate, retention is low and these processes are not effective in removing xenobiotics sustainably.

Solution pH affects the extent of xenobiotics adsorption. Lyko et al. [76] measured a UF retention of 36% for BPA at pH 5 and none at higher pH. Schäfer et al. [118] obtained similar UF retentions (30%) for this compound in pure water from pH 4 to 9, when BPA is neutral. These high retentions are associated with adsorption on the membrane. The UF process does not exhibit any retention capacity though once BPA dissociates at pH>9.3 (Table 1). Adsorption decreases dramatically accompanied by a decrease in retention due to charge repulsion between BPA and the membrane. Adsorption of xenobiotics is thought to occur through H-bonding which BPA loses when dissociated, also contributing to a decrease in adsorption.

It has to be noted that adsorption of xenobiotics to MF and UF membranes can lead to losses in xenobiotic analysis if polymeric filters (e.g. cellulose acetate and polyamide) are used in sample pre-treatment. Given that MF and UF retain particulates and some molecules, xenobiotics that are associated with such particulate or dissolved matter can also be retained and will be unaccounted for [86]. However, interactions of xenobiotics with particulates and molecules can be exploited to enhance the retention by MF and UF.

2.2. Solute-solute interaction and retention by MF and UF

Organics in wastewater play a role in xenobiotic retention, as they interact with xenobiotics and enhance their removal [34]. This case was illustrated by Schäfer et al. [118] in a submerged UF process where higher retentions of BPA at pH<9 are obtained in the presence of natural organic matter (NOM) compared to retentions of BPA without NOM. BPA partitions into the NOM and is better retained. At pH>9 due to charge repulsion between BPA, NOM and the membrane no enhancement of BPA retention is obtained since no adsorption and partitioning of BPA on the membrane and on NOM occurs.

When adsorption of xenobiotics on the membrane is the main retention mechanism, the presence of NOM can decrease their retention. NOM possesses hydrophobic moieties [49, 150], H-bonding capacity [102] or gel formation capacity [32, 38] and therefore adsorbs onto the membrane surface and competes for adsorbing sites with the xenobiotics. Pore blockage by NOM also causes less access for adsorption sites, decreasing the rate of adsorption and therefore decreasing retention of xenobiotics. This has been shown to happen for steroid hormones, pharmaceuticals and pesticides [23, 148, 146, 29].

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Solute-solute interactions of xenobiotics with organic compounds from water and wastewater are very compound and solution chemistry specific. Interaction and their effects on xenobiotic transport and removal are important. However mechanisms are to date poorly understood.

2.3. Hybrid processes on xenobiotics removal by large pore size membranes

Pre-treatment processes such as coagulation, adsorption, oxidation, complexation or precipitation enhance xenobiotic retention. The formation of larger complexes enhances the removal by large pore membrane processes.

Oxidation, pH adjustment or polymer assisted filtration can lead to the precipitation or complexation of metals and subsequent removal of the precipitate by MF or UF [19, 132, 114, 127, 71, 38].

Coagulation appears to be a poor treatment method for trace organics removal from aqueous solutions. No interaction of steroid hormones was obtained by Chang et al. [22] and Bodzek and Dudziak [16] when mixed with iron and aluminium based coagulants. The reason for this low efficiency is most likely a lack in affinity for inorganic solids as well as the low concentration of xenobiotics.

Considering sorption of steroid hormones on activated carbon (AC) is generally high [22, 16], combining MF to remove AC with the sorbed xenobiotic from solution is an option. Chang et al. [22] obtained an estrone removal as high as 96%, providing a minimum AC dosage is met.

In real life applications xenobiotics removal enhancement by hybrid MF and UF processes is a difficult task. These processes rely on an effective interaction between xenobiotics and the sorbent. This interaction depends on sorbent and xenobiotic characteristics and the solution chemistry that may both enhance or hinder the process. This makes such processes inherently complex and unlikely to function effectively for a vast number of xenobiotics or solution chemistries. A physical separation such as NF and RO is therefore an attractive option.

2.4. Xenobiotics removal using membrane bioreactors

The combination of MF/UF with biological degradation into a single process is called an MBR, considered to be a MF/UF hybrid process. Suspended solids and microorganisms responsible for biodegradation are separated from the treated water by a membrane filtration unit. In this case a biological rather than a physico-chemical process is coupled with the membrane filter. The inhibitive end product of the bioconversion by enzymes and microorganisms is continuously removed to proceed with the reaction [77, 84].

MBR are partially effective in xenobiotics removal [60, 54]. Removal is higher when compared to conventional activated sludge processes (CASP) possibly due to a higher specific surface obtained in MBR processes [58, 76]. Kim et al. [62] obtained >95% removal of hormones and some pharmaceuticals (e.g. ibuprofen) by treating wastewater from University campus dormitories and student apartments. Xenobiotics removal can be effective if they are biodegraded after an association with the biomass in the MBR which is obtained for contaminants such as BPA, nonylphenol (NP), pharmaceuticals and endocrine disrupting chemicals (EDC) [27]. Removal is also effective when the xenobiotic adsorbs on the biomass suspended solids [59, 60] and is later separated from the treated water by MF or UF. Adsorption on the sludge is found to be the highest at lower pH where there is less charge repulsion between the sludge and the xenobiotics [117, 81]. Removal is also enhanced for xenobiotics with lower dipole moment or higher hydrophobicity [13, 54]. Due to gel formation or fouling on the membrane surface there is thought to be a shift of the membrane MWCO which can partly remove macromolecular organic carbon to which xenobiotics are adsorbed to [117, 76, 81].

However removal of compounds such as CBZ and SMX has been found to be very low or nonexistent for MBR and conventional processes due to a low sorption capacity on the sludge [27, 60, 44, 62, 109].

Xenobiotics that are not removed are discharged and in consequence often found in natural waters [50, 108] or in river, ocean and soil sediments [73, 139, 18]. Degradation of compounds into smaller, more hydrophilic, polar, persistent and sometimes more toxic molecules also occurs and is to date poorly understood [13, 44, 54]. For example Hu et al. [54] obtained higher concentrations of NP in the effluent compared to the influent concentration due to NP production from parent compounds. Although MBR processes show enhanced xenobiotics removal compared to conventional treatment processes, this removal is still insufficient and poorly understood.

3 Nanofiltration and reverse osmosis

NF pores are in the <2 nm range while RO “pores” are to be seen as non-discernable voids between polymer chains. Transport of a liquid through a dense membrane is described in terms of the solution-diffusion mechanism which is a function of solubility on the membrane and its diffusivity. Each permeant dissolves in the membrane material and passes by diffusion due to its chemical potential gradient [15]. In NF the transport of liquid through the membrane is considered to be between UF and RO with a contribution of both convection and sorption-diffusion.

The retention of contaminants by NF and RO membranes involves several mechanisms such as steric exclusion, adsorption followed by diffusion and electrostatic interactions. These mechanisms depend on the membrane properties such as surface charge and pore size, the xenobiotic properties such as H-bonding capacity, molecular size and polarity and the solution chemistry involved such as pH, ionic strength and the presence of NOM.

A simplified schematic of the several mechanisms involved in xenobiotics retention by NF and RO membranes is shown in Figure 3.

FIGURE3

3.1. Size exclusion

Size exclusion mechanism is directly related with molecular size. In general it increases with increase of compound MW [14, 35, 64] and retentions are usually higher than 90% [112, 111, 138, 62, 69] for compounds with MW higher than the MWCO of the membrane [14, 136, 70] (see Figure 4A). MW has been shown to be a good indicator of the retention trend obtained by NF and RO membranes compared to other molecular sizes, e.g. Stokes diameter [136].

FIGURE4

However, this trend is not always obeyed and deviations occur in NF and RO (see Figure 4). For NF this happens especially when the contaminant size is of the same order as the membrane pores [65] (see Figure 4A). The retention is affected by the occurrence of adsorption phenomena, charge interactions between the contaminant and the membrane material and the presence of a third component in solution such as NOM. Presence of ions such as monovalent and divalent salts also affects retention.

3.2. Adsorption

Many polymeric membranes adsorb xenobiotics. Adsorptions of pesticides, steroid hormones, volatile organic carbon (VOCs) and pharmaceuticals of up to 100% are obtained [24, 35, 66, 96, 64, 119, 65, 87, 148, 93, 106, 151, 70, 97].

Adsorption plays an important role in membrane retention. Until saturation of the membrane sites is achieved the real retention is overestimated [63, 64, 91]. While adsorption occurs, the apparent retention is often >90% but once the membrane becomes saturated this latter decreases drastically, sometimes to <10% [63, 64, 55, 56, 80]. The permeate concentration shows a

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breakthrough curve similar to an AC process, with a slow increase in the initial phase until it reaches equilibrium translated in a constant permeate concentration with time (see Figure 5A). This is accompanied by a feed concentration decrease until saturation occurs. In this later phase steric hindrance and electrostatic interactions as well as solution diffusion govern retention.

However contaminants such as SMX and CBZ do not show any breakthrough curve during filtration (see Figure 5B) where adsorption on the membrane does not occur. Retention is mainly governed by size exclusion and charge interactions.

FIGURE 5

Besides giving apparent retention values at initial stages of filtration, adsorption also causes the accumulation of important amounts of xenobiotics on the membrane polymers which can be of significant risk in water treatment. Release of high concentrations of xenobiotics that are sorbed on the membrane may occur during the periodical cleaning procedure of the membranes and hence contaminate the water where it is discharged to [92]. Changes in solution pH causing the contaminant to dissociate and desorb can also occur, where both permeate and feed concentration become contaminated. It is therefore important to understand how adsorption occurs and what governs it. Adsorption on the membrane is highly dependent on the membrane material used [66, 63], the contaminant and their properties. The solution chemistry, such as pH and ionic strength, also affects adsorption on the membranes.

When comparing adsorption of SMX, estrone, BPA, fluoranthene and CBZ the latter four show much higher adsorptions on NF and RO membranes at neutral pH [148, 146, 29].

Since SMX and the membrane are both negatively charged at neutral pH, charge repulsion occurs and no adsorption is obtained. SMX is also more hydrophilic compared to other contaminants so sorptive interactions are not favoured [94]. As a general trend, the more hydrophobic the compound is the more it will adsorb on the membrane [66, 148, 93, 95, 146, 29, 147] since this requires less free energy compared to forming a “cavity” in the water phase [45].

It is argued that sorption interactions between the membrane and trace contaminants occur through H-bonding capacity which is lost for some contaminants when they dissociate (e.g. BPA). When SMX dissociates it does not lose its full H-bonding capacity due to $–SO_2$, $–NH_2$, –N, -O and the benzene groups (Table 1) However no adsorption occurs for SMX. Charge repulsion and hydrophilicity overcome the H-bonding capacity and SMX does not adsorb when compared to estrone for example [70]. Adsorption between the membrane and SMX could occur at low pH, when the compound is neutral and charge repulsion does not take place. However, SMX adsorption is negligible for a membrane of the same polymer material [95]. It is striking that compared to other bipolar molecules, SMX although capable does not form H-bonding with the membrane material. Being highly hydrophilic SMX does not need to bind with a hydrophobic membrane to be stable in solution.

CBZ adsorbs less when compared to estrone and BPA [29]. Although estrone and CBZ are both bipolar and possess =O groups, estrone adsorbs more. CBZ is neutral so charge repulsion does not play any role. On the other hand, as SMX, CBZ is more hydrophilic which might explain the lower interaction with the membrane [94].

Fluoranthene readily adsorbs on the membrane when compared to estradiol [148] although it does not possess any strong H-bonding groups. However, fluoranthene is the most hydrophobic of the studied contaminants (Log K_{ow} of 5.2 in Table 1) and adsorbs therefore on the membrane showing the influence of hydrophobic interactions on adsorption [89]. This was also shown in the study by Chang et al. [23] where high adsorption of estrone is obtained on a polypropylene membrane. Since this material is not able to form H-bonds, hydrophobicity explains the strong adsorption.

Estrone and BPA have similar size, Log K_{ow} and pK_a (Table 1) and both readily adsorb on the membrane although estrone has higher adsorption. This adsorption causes lower retentions than expected for membranes with smaller pores than the compound [64] due to diffusion of the xenobiotic through the membrane. The main difference between estrone and BPA is in their molecular structure. Estrone and BPA are bipolar, although estrone has one =O, one benzene ring

and one -OH and BPA has only two -OH and two benzene rings. The =O group forms stronger H-bonds than the -OH group explaining the higher adsorption of estrone compared to BPA. This was showed by Neale *et al*. [85] when studying the interaction between hormones and organic matter. Estrone and progesterone bind more than estradiol and testosterone due to their =O groups in the molecule which are very strong H-acceptors.

Commercial membranes are usually thin film composite membranes (TFC) with a very thin active layer and a support layer made of a different material. The active layer is the selective layer with pores in the nm level and the support layer with wider pores does not give any resistance to flux. Most commercial membranes have a polyamide active layer and a polysulphone support layer although cellulose acetate active layers are also found. No comprehensive study has been made on what material adsorption occurs onto. According to McCallum et al. [80] adsorption of estradiol occurrs mainly in the polysulphone layer compared to the polyamide layer. When looking at Figure 6 one can see that H-bonding between the bipolar estradiol molecule can be formed in both layers. A high adsorptive interaction between BPA, another bipolar contaminant, was also noticed by Lyko et al. [76] with a polyethersulphone membrane. Williams et al. [141] on the other hand obtained a higher adsorption of organic pollutants such as 2-chlorophenol on the polyamide layer when compared to the polysulphone layer showing that interactions are compound and membrane material specific.

FIGURE6

Operational conditions such as flow and pressure can also affect xenobiotics adsorption. When comparing batch adsorption (membrane exposed to xenobiotic without pressure) with adsorption obtained in pressurised experiments, higher adsorption and lower extraction is obtained in the latter showing adsorption occurs either inside the pores [63, 103] or is enhanced by pressure.

Metals, ions and saccharides retentions tend to increase with pressure in NF and RO, e.g. uranium, magnesium and raffinose [122, 33, 17, 40], while the opposite is noticed for some xenobiotics and organic molecules, e.g. with sucrose [43], hormones [91, 138], pesticides [14, 144], VOCs [35], EDCs [42] and pharmaceuticals [144]. This phenomenon has not been well explained, but it is thought to be related with the adsorptive interactions that occur between the contaminants and the membrane that can lead to diffusion.

3.3. Charge repulsion

The surface charge of commercial membranes becomes more negative with increase of pH [36, 25, 119, 94, 55]. Xenobiotics that dissociate, do so at the pH corresponding to their pK_a (e.g. estrone at pH>10.3). When this occurs, charge repulsion between the membrane surface charge and the dissociated compound occur enhancing the retention of the xenobiotic [136, 63, 64, 93, 94, 144, 95, 145, 80]. This effect is especially pronounced with molecules smaller than the pore size of the membrane. For example, Berg et al. [14] obtained an increase in the pesticide mecoprop rejection from 10% to 90% when increasing the pH from 3 to 7. Solution pH can also affect pore size due to repulsion of negatively charged groups on the membrane polymer or due to membrane structural changes which in turn affect the rejection of xenobiotics [14, 3].

CBZ retention does not vary much with pH as can be seen in Figure 7. This compound is neutral and governed by steric interactions only [94]. In the previous section it was shown that this compound does not adsorb. SMX which practically does not adsorb either on the other hand changes from neutral to negatively charged at pH 5.6. Retention increases from 20% to 100% with increase of pH due to charge repulsion between the membrane and the compound (see Figure 7). Although CBZ is smaller, when these two compounds are both neutral (pH<5.6) SMX is significantly less retained. The authors explained this is due to differences in dipole moment where a higher dipole moment for the SMX causes a lower retention, as argued by other authors for different compounds [24, 135, 136, 42, 94, 95, 146]. Molecules with high dipole moment are directed towards the pore with the side of the dipole with opposite charge closer to the membrane pore, entering more easily into the membrane [24]. Kimura et al. [65] however found that a higher

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dipole moment enhances retention when a cellulose acetate membrane is used instead of a polyamide membrane as Van der Bruggen et al. [136] used in their study. Retention of polar and non-polar compounds is therefore affected by the membrane material used and no generalised trend can be obtained at present.

Although estrone is also negatively charged at high pH an opposite trend compared to SMX was obtained by Schäfer et al. [119]. When estrone dissociates at higher pH, retention decreases dramatically from >90% to 50%. Neutral estrone adsorbs on the membrane and gives an apparent high rejection. At higher pH when the molecule dissociates, charge repulsion occurs, decreasing adsorption and consequently retention. These results with estrone seem to contradict what Hu et al. [55] obtained, where estrone retention increases from 15% to 25% with increase of pH once the membrane is saturated in estrone (see Figure 7). This is caused by charge repulsion between the membrane and estrone. In the latter case the membrane was saturated with estrone which did not occur in the study by Schäfer et al. [119]. Another possible explanation for this discrepancy is the different membranes used. Although both polyamide they can have different properties which are propriety of the manufacturer.

FIGURE7

Nghiem et al. [93] showed an increase of BPA retention with pH (see Figure 7) following the same trend as SMX [94] and estrone [55]. When BPA dissociates at high pH it loses its H-bonding capacity, which only remains through the benzene ring, a weak H-acceptor. No adsorption is therefore expected to occur and retention increases due to charge repulsion.

Although most studies are focused on xenobiotics that become negatively charged and are repelled by the membrane, Heijman et al. [51] and Pronk et al. [106] showed that attraction between the negative membrane and positively charged xenobiotics translates into lower retentions. However Radjenovic et al. [110] obtained rejections >90% for positively charged pharmaceuticals in a Spanish drinking water treatment plant.

The increase of ionic strength in solution decreases membrane rejection of charged compounds due to charge shielding between the membrane and the contaminant [122, 39, 95, 40], with calcium ions shielding more effectively than sodium ions [95]. Zhang et al. [151] also showed a decrease in BPA rejection with increase of ionic strength due to swelling of the membrane pores or due to a decrease in the BPA hydrodynamic radius.

As with charged organic xenobiotics metals and heavy metals are mainly removed through the Donnan exclusion mechanism where the metal ion with the same charge as the membrane has a retention higher than 80% [111, 39] due to charge repulsion [111, 99, 122, 26, 40]. Metal speciation study is therefore important to understand the rejection mechanisms not only due to different charges the metal species carry but also due to different species the metal can form e.g. with carbonates and NOM, which affects its size and therefore its retention.

While many studies on the retention of xenobiotics by NF/RO exist, mechanisms are to date not fully understood and hence it is difficult to predict the removal of a particular xenobiotic correctly. The presence of another compound in water renders this prediction even more difficult due to several types of interactions that take place.

3.4. Solute-solute interactions and fouling

Although MW is still a good guidance to predict retention by the membrane, the solution characteristics where the contaminant is found in, such as presence of NOM, can affect the retention and overcome the size exclusion prediction.

3.4.1 Solute-solute interaction with retained organics increases xenobiotics retention

When NOM is present in solution enhanced retention is generally obtained for xenobiotics [1, 34, 91, 93, 144, 56, 70, 110] due to partitioning of the contaminant into the retained NOM [103, 106]. Agbekodo et al. [1] showed that increasing organic carbon concentration from 2 to 2.8 mg/L increases pesticide removal from 67% to 90%.

3.4.2 Absence of solute-solute interaction of xenobiotics with retained organics does not affect xenobiotic retention

Certain types of NOM, e.g. surfactants, are found not to affect xenobiotics retention [14, 91, 56], showing that the nature of NOM plays a fundamental role in NOM-contaminant interaction and consequent retention by the membrane. According to Neale et al. [85] estradiol bounds less to surfactants because partitioning is expected to occur through weak H-bonding with the hydrophilic surfactant head in contrast with other types of NOM, such as humic acid, which form stronger H-bonding.

3.4.3 Membrane fouling increases xenobiotics retention

Fouling by NOM modifies the membrane surface and pore properties and affects the retention of small compounds [103, 145] especially for NF membranes when compared to RO [28]. NOM can block the membrane pores or change the membrane surface properties enhancing contaminant removal by steric exclusion and charge repulsion [106, 51, 56, 69, 90, 28, 80, 89, 97].

3.4.4 Membrane fouling decreases xenobiotics retention

A decrease in xenobiotics retention as a consequence of fouling can also occur. NOM adsorption and increase in membrane negative surface charge increases the MWCO of the membrane due to charge repulsion between the functional groups on the membrane [145] resulting in lower rejection of ionic solutes.

Colloidal fouling also causes a decrease in xenobiotics retention by NF and RO membranes [87, 89]. Due to the cake formed on the membrane surface, back diffusion to the feed is hindered which causes accumulation on the membrane surface and consequent diffusion through the membrane polymer [2, 90, 97].

Other types of foulant decrease the membrane surface charge when adsorbed, decreasing the repulsion between the membrane and the xenobiotic [51, 90].

3.4.5 Membrane fouling affects xenobiotics adsorption

When NOM is present two main trends are found in the xenobiotic adsorption mechanism on membranes. Higher adsorption of the contaminant is obtained, possibly on both membrane and NOM layer that is formed on the membrane surface [1, 96, 145, 55, 56]. In the case of hydrophobic HA presence for example, it renders the membrane more hydrophobic, enhancing estrone adsorption [55, 56]. Jin et al. [56] found that estrone interaction with NOM depends on the NOM specific functional groups, such as the presence of phenolic groups, which enhance estrone retention by partitioning into the NOM, but do not seem to readily affect estrone adsorption on the membrane.

On the other hand, a decrease in xenobiotics adsorption also occurs when there is competition between the NOM and the contaminant for adsorbing sites [148, 103, 146, 151, 80, 89, 97]. Competition for adsorption between different xenobiotics also take place [66, 103] decreasing the retention when compared to a single xenobiotic solution.

Complexity of natural waters renders the removal prediction of xenobiotics difficult due to all the interactions that take place between the xenobiotic, the compounds in water and the membrane. Removal mechanisms are to date poorly understood.

Studies on the removal of xenobiotics by membranes not involving pressure driven processes are scarcer because water treatment applications are currently dominated by pressure driven processes. From the studies presented next it can be seen though that membrane processes share some of the mechanisms of xenobiotics removal such as adsorption followed by diffusion through the membrane material amongst others. They depend on the contaminant chemical characteristics, e.g. hydrophobicity.

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4 Electrodialysis

Ions or charged molecules can be removed by ED where an electrical potential difference acts as the driving force for separation. Uncharged compounds are unaffected and can be separated from charged compounds. Electrically charged membranes (cation-exchange membranes allow the passage of cations and anion-exchange membranes allow the passage of anions [84]) are alternately stacked between the positive electrode (anode) and negative electrode (cathode). Cations migrate to the cathode and anions migrate to the anode [126]. Two phases are obtained: the diluate which is purified and free from charged solutes and the concentrate where the charged solutes migrate to and concentrate.

ED studies have mainly focused on wastewater treatment of metals and heavy metals from industrial wastewaters [78, 75]. In general, high removals of metals are achieved by this process although membrane type affects metal removal [46, 134, 8, 130, 9]. Metal speciation plays an important role. In some cases the pH of the solution has to be adjusted and/or controlled since it affects the metal solubility, charge and therefore the metal mobility [46, 79, 78, 130].

Less attention has been given on the application of ED for the removal of xenobiotics, despite the fact that some deprotonate at a certain pH and could be removed. The only studies are on the applicability of ED for salts recovery from a urine solution containing xenobiotics [37, 105]. Although high removal of 17α-ethinylestradiol is obtained [37], Pronk et al. [105] showed that xenobiotics such as CBZ and propanolol readily adsorb on the membranes, where electrostatic, size exclusion and hydrophobic interactions play a role in the adsorption behaviour. More hydrophobic compounds seem to adsorb more. This adsorption governs the permeation of these contaminants through the ED membranes since both increase with time and breakthrough eventually occurs. Pronk et al. [107] studied the application of ED followed by ozonation in a pilot scale for the production of a fertiliser from urine. Whilst the conductivity decreases substantially to almost 100% removal of salts, all xenobiotics are below detection limit with the exception of ibuprofen. Ibuprofen adsorbs on the membrane and, after saturation of the membrane sites, significant permeation occurs.

5 Pervaporation

In PV the permeate is removed as vapour from the feed stream in contact with a dense hydrophobic membrane due to a low vapour pressure on the permeate side.

This process was first applied in the removal study of VOCs. Most xenobiotics such as EDCs have low volatility, high MW and low water solubility when compared to VOCs. Although PV does not seem to be an appropriate treatment process it has been applied for the treatment of water containing trace amounts of xenobiotics. According to Higuchi et al. [53] removal of trace amounts of EDCs is >90% and a function of the contaminant hydrophobicity. A high removal by more hydrophobic compounds was also obtained by other authors [98, 52]. Interactions between the contaminant and the membrane are crucial in the removal performance by PV [98].

However, due to the xenobiotics low vapour pressure and high MW when compared to VOCs, the driving force needs to be enhanced to increase removal rates [52, 133], translating into higher energy requirements.

Contrary to NF and RO, in PV the higher the interaction of the xenobiotic with the membrane the better, since the contaminant is to be removed on the permeate side. The more hydrophobic compounds permeate better, but in general xenobiotics have large MW and low vapour pressures, translating into a higher driving force, accompanied by energy costs.

6 Membrane Distillation

In a MD process two liquids at different temperatures are separated by a very hydrophobic microporous membrane. This temperature difference results in a vapour pressure gradient, the

driving force for separation. Thus transport occurs by evaporation on the high-temperature side followed by transport of the vapour molecules through the membrane pores. Finally the molecule condenses on the permeate side which is either a liquid or a gas at a lower temperature [84, 30].

The application of MD to xenobiotic contaminated water is appealing since most xenobiotics have low vapour pressures and the solution they are found in can be concentrated, with pure water obtained on the permeate side. Wu et al. [143] studied the application of MD in the treatment of a taurine rich pharmaceutical wastewater effluent where the concentrate obtained is very rich in taurine (66% purity). Cartinella et al. [21] studied the removal of natural steroid hormones using MD. Rejections of estrone and estradiol are >99.5% without having much affect on the water recovery. Solutions containing urine and humidity condensate with trace amounts of organic acids do not affect the performance either and rejections are maintained >99.5%. Zolotarev et al. [152] studied the removal of heavy metals from wastewater and obtained a pure distillate of water and a heavy metal selectivity of 99.8% which only decreased to 99.7% when the feed metal concentration increased. MD can therefore be used to very high concentrations of metals without losing its selectivity. However, this is accompanied with a decrease in trans-membrane flux.

MD can also be used by applying vacuum on the permeate side (vacuum membrane distillation) to remove volatile xenobiotics from the feed solution. Couffin et al. [30] and Banat et al. [10] showed that MD can be used to remove halogenated VOCs and benzene (87% removal) from water, respectively.

7 Large Scale Applications

Despite the pessimistic picture previously painted in the efficiency of xenobiotics removal by membrane processes, large scale applications have shown very good results with high water quality obtained. These applications are motivated by the need to remove xenobiotics for water treatment where the water supply is contaminated, or for water recycling where wastewater is treated to a potable water standard. Increasing water pollution awareness combined with increased water demand and water scarcity is rapidly expanding the number of large scale plants. A number of such applications will be outlined here.

- Méry sur Oise

The Méry-sur-Oise water purification plant in Paris, France, treats water for potable usage directly from the river Oise to 650,000 people with a daily maximum production of 340,000 m^3. The majority of the treated water produced (80%) originates from MF pre-treatment followed by NF treatment, while the remaining (20%) originates from conventional biological treatment. The NF area used is 340,000 m^2, corresponding to 9,120 modules of Dow Filmtec NF 200 membranes (polyamide on a polysulphone support and polypripazine as an ultrathin top layer). The choice of the membrane technology was due to its high removal of organic carbon and pesticides when compared to conventional processes [137, 31].

The Oise generally has very high concentrations of pesticides (e.g. >1.6 µg/L in May, June and August of 2007 [123]). The highest concentrations were measured for glyphosate and aminomethyll phosphon acid (AMPA) ranging from 0.2 µg/L to 0.9 µg/L. Removal of pesticides remains very high with single pesticide concentration lower than 0.1 µg/L and 0.5 µg/L for total pesticide concentration in the treated water. In 2007 the atrazine and desethylatrazine concentrations in treated water were always lower than the detection limit of 50 ng/L [124].

The total organic carbon (TOC) removal is also very high with a drinking water concentration of about 2 mg/L (2007). Disinfection by-products (DBP) such as trihalomethanes are removed in the process to concentrations lower than 90 µg/L. Metals such as aluminium have concentrations lower than 12 µg/L in the treated water [124].

- NEWater

The NEWater facilities in Singapore are advanced water reclamation plants designed to produce a total of 75,000 m^3/day of water [129] with MF followed by RO and UV disinfection. The water influent originates from a clarified secondary effluent with CASP. This treated water can be

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further reused as high grade industrial water (e.g. microelectronics industry) or for indirect potable reuse applications. For a typical input of 12 mg/L of TOC removals higher than 99% were achieved in 2000 [121]. Sample analyses from 2000 to 2002 showed concentrations of pesticides in the treated water lower than 0.1 µg/L and of DBP lower than 75.9 µg/L [125].

- Water Factory 21 (WF21)

WF21 in California, USA, was built to treat and purify wastewater from the Orange County District to drinking water standards. This treated water was then injected into the groundwater basin [100] that supplies drinking water to a population of more than 2 million people. Groundwater is protected from seawater intrusion by injecting up to 19,000 m^3/day of treated reclaimed water to be blended with deep-well water into coastal aquifers. A RO treatment with Hydranautics ESPA2 polyamide membranes was added to reduce salts and organics, with MF as a pre-treatment process.

DBP such as N-Nitrosodimethylamine (NDMA) were detected in several drinking water wells in California [20]. The presence of this compound in the injected water from WF21 forced the interruption of the plant in 2000-2001, reducing water treatment by more than 85% [83]. The levels of NDMA in the discharged water were higher than 20 ng/L [82, 20]. A UV treatment was subsequently installed to remove the NDMA. According to a study by Plumlee et al. [104], the RO process in WF21 removes NDMA between 24-56%, depending on the sampling season. With the addition of UV treatment the overall removal increases up to 75%. As expected MF does not remove any of the NDMA. On the contrary, due to chlorination pre-treatment to avoid MF fouling the NDMA concentration increases in the MF influent.

Metals and heavy metals concentrations in 2003 were below 5 µg/L, organic carbon was below 0.7 mg/L and trihalomethanes were below 2.7 µg/L [140].

WF21 has stopped working since 2007 to be replaced by an improved and larger water purification plant [47, 101].

- Luggage Point Water Reclamation Plant

The Luggage Point Water Reclamation Plant (LPWRP) was built to convert effluent from a WWTP into high quality reclaimed water for industrial reuse (e.g. BP refinery cooling towers) with MF pre-treatment followed by BW30 RO membranes from Dow Filmtec (polyamide on polysulphone support). Its maximum production is 10,600 m^3/day [5].

According to a study by Al-Rifai [4] in 2006 the MF process does not reject any of the studied xenobiotics. The removal of acidic pharmaceuticals (e.g. ibuprofen) by the RO membranes on the other hand is high and varies between 30% and 100% and increases with the increase of compounds log K_{ow} and pK_a. Rejection of neutral pharmaceuticals (e.g. CBZ) ranges from 63% to 100%. For EDCs (e.g. BPA) removal varies greatly between 0% and 100%. No relationship with the compounds characteristics was found for the latter two classes of compounds.

Other membrane plants applying NF and RO processes have reported good removal of xenobiotics to very low concentrations. In the Debden Road Plant UK, pesticide concentration is lower than 0.1 µg/L in the permeate [41]. According to Khan et al. [61] RO shows the best results in removing hormones and pharmaceuticals compared to NF, UF and MF in a water recycling demonstration plant in Queensland, Australia.

Despite the high removal percentages of xenobiotics by NF/RO processes, some compounds are not readily removed and show high concentrations in the treated water (e.g. NDMA and BPA) meaning that removal by membrane processes is insufficient. Furthermore the concentrate stream obtained in these processes which is very rich in xenobiotics poses a disposal problem that needs to be addressed. Disposal of the washing solutions for both MF/UF and NF/RO processes can also present a problem since polymeric membranes are capable of adsorbing high rates of xenobiotics, which desorb under certain backwash conditions such as acidic and alkaline washes.

8 Conclusions

Xenobiotics removal by NF and RO has progressed to full scale applications in water and wastewater treatment with particular interest in water recycling applications. The key advantage of membrane filtration for xenobiotics removal is the fact that treatment is a physical process that does not result in unwanted by-products. Removal of many xenobiotics by membrane filtration is effective albeit compound and membrane specific. In fact, removal mechanisms for each process are governed by xenobiotics characteristics, membrane type, water matrix and solution chemistry (such as the presence of other xenobiotics or organics, pH and ionic strength) and operational parameters (such as pressure, feed flow rate). This makes removal prediction of specific compounds for a specific water difficult. Long term phenomena such as membrane fouling further affect xenobiotics retention which means that removal can vary with time as well as season. The underlying mechanisms for xenobiotics removal are size exclusion, adsorption followed by diffusion and charge repulsion. These mechanisms are currently not understood well enough to allow prediction of removal of xenobiotics. Different waters require a tailored process with requires individual design and pilot testing.

9 References

[1] Agbekodo, K. M., Legube, B. & Dard, S. (1996). Atrazine and simazine removal mechanisms by nanofiltration: influence of natural organic matter concentration. *Water Research*, *30*, 2535-2542.

[2] Agenson, K. O. & Urase, T. (2007). Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications. *Separation and Purification Technology*, *55*, 147-156.

[3] Ahmad, A. L., Tan, L. S. & Abd. Shukor, S. R. (2008). The role of pH in nanofiltration of atrazine and dimethoate from aqueous solution. *Journal of Hazardous Materials*, *154*, 633-638.

[4] Al-Rifai, J. H. (2008) Performance of water recycling technologies. University of Wollongong.

[5] Al-Rifai, J. H., Gabelish, C. L. & Schäfer, A. I. (2007). Occurrence of pharmaceutically active and non-steroidal estrogenic compounds in three different wastewater recycling schemes in Australia. *Chemosphere*, *69*, 803-815.

[6] Anselme, C. & Jacobs, E. P. (1996). Ultrafiltration. In J. Mallevialle, P. E. Odendaal and M. R. Wiesner (Eds.), *Water Treatment Membrane Processes*, (pp. 10.1-10.88). New York: McGraw-Hill.

[7] Aptel, P. & Buckley, C. A. (1996). Categories of membrane operations. In J. Mallevialle, P. E. Odendaal and M. R. Wiesner (Eds.), *Water Treatment Membrane Processes*, (pp. 2.1-2.24). McGraw-Hill.

[8] Banasiak, L. J., Kruttschnitt, T. W. & Schäfer, A. I. (2007). Desalination using electrodialysis as a function of voltage and salt concentration. *Desalination*, *205*, 38-46.

[9] Banasiak, L. J. & Schäfer, A. I. (2009). Removal of boron, fluoride and nitrate by electrodialysis in the presence of organic matter. *Journal of Membrane Science*, *334*, 101-109.

[10] Banat, F. A. & Simandl, J. (1996). Removal of benzene traces from contaminated water by vacuum membrane distillation. *Chemical Engineering Science*, *51*, 1257-1265.

[11] Baronti, C., Curini, R., D'Ascenzo, G., Di Corcia, A., Gentili, A. & Samperi, R. (2000). Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water. *Environmental Science & Technology*, *34*, 5059-5066.

[12] Batt, A. L., Kostich, M. S. & Lazorchak, J. M. (2008). Analysis of ecologically relevant pharmaceuticals in wastewater and surface water using selective solid-phase extraction and UPLC-MS/MS. *Analytical Chemistry*, *80*, 5021-5030.

[13] Baumgarten, S., Schröder, H. F. & Pinnekamp, J. (2006). Performance of membrane bioreactors used for the treatment of wastewater from the chemical and textile industries. *Water Science & Technology*, *53*, 61-67.

[14] Berg, P., Hagmeyer, G. & Gimbel, R. (1997). Removal of pesticides and other micropollutants by nanofiltration. *Desalination*, *113*, 205-208.

[15] Bitter, J. G. A. (1991). *Transport Mechanisms in Membrane Separation Processes*. New York: Plenum Press.

[16] Bodzek, M. & Dudziak, M. (2006). Elimination of steroidal sex hormones by conventional water treatment and membrane processes. *Desalination*, *198*, 24-32.

[17] Bowen, W. R. & Welfoot, J. S. (2005). Modelling the performance of nanofiltration membranes. In A. I. Schäfer, A. G. Fane and T. D. Waite (Eds.), *Nanofiltration: Principles and Applications*, (pp. 119-146). Oxford: Elsevier.

[18] Braga, O., Smythe, G. A., Schäfer, A. I. & Feitz, A. J. (2005). Steroid estrogens in ocean sediments. *Chemosphere*, *61*, 827-833.

Semião, A.J.C. ; Schäfer, A.I. (2010) Xenobiotics removal by membrane technology: An overview,
(In) Xenobiotics in the Urban Water Cycle: Mass Flows, Environmental Processes and Mitigation Strategies, Bester, K. ; Kümmerer, K. ; Fatta-Kassinos, D. (Eds)
Springer Environmental Book Series, Environmental Pollution, Vol. 16,
Springer, Hardcover, ISBN: 978-90-481-3508-0, 480 pp.

[19] Broom, G. P., Squires, R. C., Simpson, M. P. J. & Martin, I. (1994). The treatment of heavy metal effluents by crossflow microfiltration. *Journal of Membrane Science*, *87*, 219-230.
[20] California Department of Public Health, (2006) A brief history of NDMA findings in drinking water, Retrieved March 17, 2009 from http://www.cdph.ca.gov/certlic/drinkingwater/Pages/NDMAhistory.aspx.
[21] Cartinella, J. L., Cath, T. Y., Flynn, M. T., Miller, G. C., Hunter, K. W. & Childress, A. E. (2006). Removal of natural steroid hormones from wastewater using membrane contactor processes. *Environmental Science & Technology*, *40*, 7381-7386.
[22] Chang, S., Waite, T. D., Ong, P. E. A., Schäfer, A. I. & Fane, A. G. (2004). Assessment of trace estrogenic contaminants removal by coagulant addition, powdered activated carbon adsorption and powdered activated carbon/microfiltration processes. *Journal of Environmental Engineering*, *130*, 736-742.
[23] Chang, S., Waite, T. D., Schafer, A. I. & Fane, A. G. (2003). Adsorption of the endocrine-active compound estrone on microfiltration hollow fiber membranes. *Environmental Science & Technology*, *37*, 3158-3163.
[24] Chian, E. S. K., Bruce, W. N. & Fang, H. H. P. (1975). Removal of pesticides by reverse osmosis. *Environmental Science & Technology*, *9*, 52-59.
[25] Childress, A. E. & Elimelech, M. (1996). Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*, *119*, 253-268.
[26] Choo, K. H., Kwon, D. J., Lee, K. W. & Choi, S. J. (2002). Selective removal of cobalt species using nanofiltration membranes. *Environmental Science and Technology*, *36*, 1330-1336.
[27] Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. & Kroiss, H. (2005). Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Research*, *39*, 4797-4807.
[28] Comerton, A. M., Andrews, R. C., Bagley, D. M. & Hao, C. (2008). The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties. *Journal of Membrane Science*, *313*, 323-335.
[29] Comerton, A. M., Andrews, R. C., Bagley, D. M. & Yang, P. (2007). Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds. *Journal of Membrane Science*, *303*, 267-277.
[30] Couffin, N., Cabassud, C. & Lahoussine-Turcaud, V. (1998). A new process to remove halogenated VOCs for drinking water production: vacuum membrane distillation. *Desalination*, *117*, 233-245.
[31] Cyna, B., Chagneau, G., Bablon, G. & Tanghe, N. (2002). Two years of nanofiltration at the Méry-sur-Oise plant, France. *Desalination*, *147*, 69-75.
[32] Davis, T. A., Volesky, B. & Mucci, A. (2003). A review of the biochemistry of heavy metal biosorption by brown algae. *Water Research*, *37*, 4311-4330.
[33] de Pinho, M. N., Semião, V. & Geraldes, V. (2002). Integrated modeling of transport processes in fluid/nanofiltration membrane systems. *Journal of Membrane Science*, *206*, 189-200.
[34] Devitt, E. C., Ducellier, P. C., Cote, P. & Wiesner, M. R. (1998). Effects of natural organic matter and the raw water matrix on the rejection of atrazine by pressure-driven membranes. *Water Research*, *32*, 2563-2568.
[35] Ducom, G. & Cabassud, C. (1999). Interests and limitations of nanofiltration for the removal of volatile organic compounds in drinking water production. *Desalination*, *124*, 115-123.
[36] Elimelech, M., Chen, W. H. & Waypa, J. J. (1994). Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer. *Desalination*, *95*, 269-286.
[37] Escher, B. I., Pronk, W., Suter, M. J. F. & Maurer, M. (2006). Monitoring the removal efficiency of pharmaceuticals and hormones in different treatment processes of source-separated urine with bioassays. *Environmental Science & Technology*, *40*, 5095-5101.
[38] Fatin-Rouge, N., Dupont, A., Vidonne, A., Dejeu, J., Fievet, P. & Foissy, A. (2006). Removal of some divalent cations from water by membrane-filtration assisted with alginate. *Water Research*, *40*, 1303-1309.
[39] Favre-Reguillon, A., Lebuzit, G., Foos, J., Guy, A., Draye, M. & Lemaire, M. (2003). Selective concentration of uranium from seawater by nanofiltration. *Industrial & Engineering Chemistry Research*, *42*, 5900-5904.
[40] Favre-Reguillon, A., Lebuzit, G., Murat, D., Foos, J., Mansour, C. & Draye, M. (2008). Selective removal of dissolved uranium in drinking water by nanofiltration. *Water Research*, *42*, 1160-1166.
[41] Gaid, A., Bablon, G., Turner, G., Franchet, J. & Christophe Protais, J. (1998). Performance of 3 years operation of nanofiltration plants. *Desalination*, *117*, 149-158.
[42] Gallenkemper, M., Wintgens, T. & Melin, T. (2003). Nanofiltration of endocrine disrupting compounds. *Water Science and Technology: Water Supply*, *3*, 321-327.
[43] Geraldes, V., Semiao, V. & Norberta de Pinho, M. (2002). The effect on mass transfer of momentum and concentration boundary layers at the entrance region of a slit with a nanofiltration membrane wall. *Chemical Engineering Science*, *57*, 735-748.
[44] Göbel, A., McArdell, C. S., Joss, A., Siegrist, H. & Giger, W. (2007). Fate of sulfonamides, macrolides, and trimethoprim in different wastewater treatment technologies. *Science Of The Total Environment*, *372*, 361-371.
[45] Goss, K. & Schwarzenbach, P. (2003). Rules of thumb for assessing equilibrium partitioning of organic compounds: successes and pitfalls. *Journal of Chemical Education*, *80*, 450-455.
[46] Green, T. A., Roy, S. & Scott, K. (2001). Recovery of metal ions from spent solutions used to electrodeposit magnetic materials. *Separation and Purification Technology*, *22-23*, 583-590.

[47] Groundwater Replenishment System, (2004) Orange County's historic water factory 21 stops producing highly purified water, Retrieved March 17, 2009 from http://www.gwrsystem.com/news/releases/040121.html.
[48] Hansch, C., Leo, A. & Hoekman, D. (1995). *Exploring QSAR: hydrophobic, electronic, and steric constants*. Washington, DC.: American Chemical Society.
[49] Haslam, E. (1996). Natural polyphenols (vegetable tannins) as drugs: possible modes of action. *Journal of Natural Products*, *59*, 205-215.
[50] Heberer, T. (2002). Tracking persistent pharmaceutical residues from municipal sewage to drinking water. *Journal of Hydrology*, *266*, 175-189.
[51] Heijman, S. G. J., Verleifde, A. R. D., Cornelissen, E. R., Amy, G. & van Dijk, J. C. (2007). Influence of natural organic matter (NOM) fouling on the removal of pharmaceuticals by nanofiltration and activated carbon filtration. *Water Science and Technology: Water Supply*, *7*, 17-23.
[52] Higuchi, A., Yoon, B.-O., Asano, T., Nakaegawa, K., Miki, S., Hara, M., He, Z. & Pinnau, I. (2002). Separation of endocrine disruptors from aqueous solutions by pervaporation. *Journal of Membrane Science*, *198*, 311-320.
[53] Higuchi, A., Yoon, B. O., Kaneko, T., Hara, M., Maekawa, M. & Nohmi, T. (2004). Separation of endocrine disruptors from aqueous solutions by pervaporation: dioctylphthalate and butylated hydroxytoluene in mineral water. *Journal of Applied Polymer Science*, *94*, 1737-1742.
[54] Hu, J. Y., Chen, X., Tao, G. & Kekred, K. (2007). Fate of endocrine disrupting compounds in membrane bioreactor systems. *Environmental Science & Technology*, *41*, 4097-4102.
[55] Hu, J. Y., Jin, X. & Ong, S. L. (2007). Rejection of estrone by nanofiltration: Influence of solution chemistry. *Journal of Membrane Science*, *302*, 188-196.
[56] Jin, X., Hu, J. & Ong, S. L. (2007). Influence of dissolved organic matter on estrone removal by NF membranes and the role of their structures. *Water Research*, *41*, 3077-3088.
[57] Johnson, A. C. & Sumpter, J. P. (2001). Removal of endocrine-disrupting chemicals in activated sludge treatment works. *Environmental Science & Technology*, *35*, 4697-4703.
[58] Joss, A., Andersen, H., Ternes, T., Richle, P. R. & Siegrist, H. (2004). Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: consequences for plant optimization. *Environmental Science & Technology*, *38*, 3047-3055.
[59] Joss, A., Keller, E., Alder, A. C., Göbel, A., McArdell, C. S., Ternes, T. & Siegrist, H. (2005). Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research*, *39*, 3139-3152.
[60] Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C. S., Ternes, T. A., Thomsen, A. & Siegrist, H. (2006). Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. *Water Research*, *40*, 1686-1696.
[61] Khan, S. J., Wintgens, T., Sherman, P., Zaricky, J. & Schafer, A. I. (2004). Removal of hormones and pharmaceuticals in the advanced water recycling demonstration plant in Queensland, Australia. *Water Science and Technology*, *50*, 15-22.
[62] Kim, S. D., Cho, J., Kim, I. S., Vanderford, B. J. & Snyder, S. A. (2007). Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Research*, *41*, 1013-1021.
[63] Kimura, K., Amy, G., Drewes, J. & Watanabe, Y. (2003). Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection. *Journal of Membrane Science*, *221*, 89-101.
[64] Kimura, K., Amy, G., Drewes, J. E., Heberer, T., Kim, T.-U. & Watanabe, Y. (2003). Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes. *Journal of Membrane Science*, *227*, 113-121.
[65] Kimura, K., Toshima, S., Amy, G. & Watanabe, Y. (2004). Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *Journal of Membrane Science*, *245*, 71-78.
[66] Kiso, Y., Nishimura, Y., Kitao, T. & Nishimura, K. (2000). Rejection properties of non-phenylic pesticides with nanofiltration membranes. *Journal of Membrane Science*, *171*, 229-237.
[67] Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B. & Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environmental Science & Technology*, *36*, 1202-1211.
[68] Körner, W., Bolz, U., Süßmuth, W., Hiller, G., Schuller, W., Hanf, V. & Hagenmaier, H. (2000). Input/output balance of estrogenic active compounds in a major municipal sewage plant in Germany. *Chemosphere*, *40*, 1131-1142.
[69] Kosutic, K., Dolar, D., Asperger, D. & Kunst, B. (2007). Removal of antibiotics from a model wastewater by RO/NF membranes. *Separation and Purification Technology*, *53*, 244-249.
[70] Koyuncu, I., Arikan, O. A., Wiesner, M. R. & Rice, C. (2008). Removal of hormones and antibiotics by nanofiltration membranes. *Journal of Membrane Science*, *309*, 94-101.
[71] Kryvoruchko, A. P., Yurlova, L. Y., Atamanenko, I. D. & Kornilovich, B. Y. (2004). Ultrafiltration removal of U(VI) from contaminated water. *Desalination*, *162*, 229-236.
[72] Kubli-Garfias, C. (1998). Comparative study of the electronic structure of estradiol, epiestradiol and estrone by ab initio theory. *Journal of Molecular Structure: THEOCHEM*, *452*, 175-183.

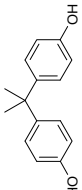
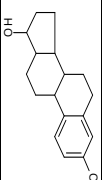
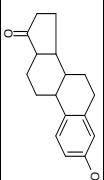
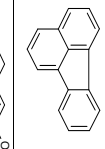
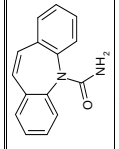
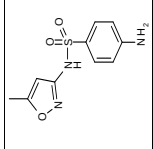
[73] Kuster, M., José López de Alda, M. & Barceló, D. (2004). Analysis and distribution of estrogens and progestogens in sewage sludge, soils and sediments. *Trends in Analytical Chemistry*, *23*, 790-798.
[74] Kwon, J. H., Liljestrand, H. & Katz, L. E. (2006). Partitioning of moderately hydrophobic endocrine disruptors between water and synthetic membrane vesicles. *Environmental Toxicology and Chemistry*, *25*, 1984-1992.
[75] Lambert, J., Avila-Rodriguez, M., Durand, G. & Rakib, M. (2006). Separation of sodium ions from trivalent chromium by electrodialysis using monovalent cation selective membranes. *Journal of Membrane Science*, *280*, 219-225.
[76] Lyko, S., Wintgens, T. & Melin, T. (2005). Estrogenic trace contaminants in wastewater - possibilities of membrane bioreactor technology. *Desalination*, *178*, 95-105.
[77] Manem, J. & Sanderson, R. (1996). Membrane bioreactors. In J. Malleviale, P. E. Odendaal and M. R. Wiesner (Eds.), *Water Treatment Membrane Processes*, (pp. 17.1-17.31). New York: McGraw-Hill.
[78] Marder, L., Bernardes, A. M. & Zoppas Ferreira, J. (2004). Cadmium electroplating wastewater treatment using a laboratory-scale electrodialysis system. *Separation and Purification Technology*, *37*, 247-255.
[79] Marder, L., Sulzbach, G. O., Bernardes, A. M. & Ferreira, J. Z. (2003). Removal of cadmium and cyanide from aqueous solutions through electrodialysis. *Journal of the Brazilian Chemical Society*, *14*, 610-615.
[80] McCallum, E. A., Hyung, H., Do, T. A., Huang, C.-H. & Kim, J.-H. (2008). Adsorption, desorption, and steady-state removal of 17β-estradiol by nanofiltration membranes. *Journal of Membrane Science*, *319*, 38-43.
[81] Melin, T., Jefferson, B., Bixio, D., Thoeye, C., De Wilde, W., De Koning, J., van der Graaf, J. & Wintgens, T. (2006). Membrane bioreactor technology for wastewater treatment and reuse. *Desalination*, *187*, 271-282.
[82] Mitch, W. A., Gerecke, A. C. & Sedlak, D. L. (2003). A N-Nitrosodimethylamine (NDMA) precursor analysis for chlorination of water and wastewater. *Water Research*, *37*, 3733-3741.
[83] Mitch, W. A., Sharp, J. O., Trussel, R. R., Valentine, R. L., Alvarez-Cohen, L. & Sedlak, D. L. (2003). N-Nitrosodimethylamine (NDMA) as a drinking water contaminant: a review. *Environmental Engineering Science*, *20*, 389-404.
[84] Mulder, M. (1996). *Basic principles of membrane technology*. Dordrecht: Kluwer Academic Publishers.
[85] Neale, P. A., Escher, B. I. & Schäfer, A. I. (2008). Quantification of solute-solute interactions using negligible-depletion solid-phase microextraction: measuring the affinity of estradiol to bulk organic matter. *Environmental Science & Technology*, *42*, 2886-2892.
[86] Neale, P. A. & Schäfer, A. I. (2009). The influence of pH on losses of analyte estradiol in sample pre-filtration. *Environmental Engineering Science*, (*in press*) DOI:10.1089/ees.2008.0291.
[87] Ng, H. Y. & Elimelech, M. (2004). Influence of colloidal fouling on rejection of trace organic contaminants by reverse osmosis. *Journal of Membrane Science*, *244*, 215.
[88] Nghiem, L. D. (2005) Removal of emerging trace organic contaminants by nanofiltration and reverse osmosis. PhD, University of Wollongong.
[89] Nghiem, L. D. & Coleman, P. J. (2008). NF/RO filtration of the hydrophobic ionogenic compound triclosan: Transport mechanisms and the influence of membrane fouling. *Separation and Purification Technology*, *62*, 709-716.
[90] Nghiem, L. D. & Hawkes, S. (2007). Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size. *Separation and Purification Technology*, *57*, 176-184.
[91] Nghiem, L. D., Manis, A., Soldenhoff, K. & Schäfer, A. I. (2004). Estrogenic hormone removal from wastewater using NF/RO membranes. *Journal of Membrane Science*, *242*, 37-45.
[92] Nghiem, L. D. & Schäfer, A. I. (2006). Critical risk points of nanofiltration and reverse osmosis processes in water recycling applications. *Desalination*, *187*, 303-312.
[93] Nghiem, L. D., Schäfer, A. I. & Elimelech, M. (2005). Nanofiltration of hormone mimicking trace organic contaminants. *Separation Science and Technology*, *40*, 2633-2649.
[94] Nghiem, L. D., Schäfer, A. I. & Elimelech, M. (2005). Pharmaceutical retention mechanisms by nanofiltration membranes. *Environmental Science & Technology*, *39*, 7698-7705.
[95] Nghiem, L. D., Schäfer, A. I. & Elimelech, M. (2006). Role of electrostatic interactions in the retention of pharmaceutically active contaminants by a loose nanofiltration membrane. *Journal of Membrane Science*, *286*, 52-59.
[96] Nghiem, L. D., Schäfer, A. I. & Waite, T. D. (2002). Adsorption of estrone on nanofiltration and reverse osmosis membranes in water and wastewater treatment. *Water Science & Technology*, *46*, 265-272.
[97] Nghiem, L. D., Vogel, D. & Khan, S. (2008). Characterising humic acid fouling of nanofiltration membranes using bisphenol A as a molecular indicator. *Water Research*, *42*, 4049-4058.
[98] Nguyen, T. Q. & Nobe, K. (1987). Extraction of organic contaminants in aqueous solutions by pervaporation. *Journal of Membrane Science*, *30*, 11-22.
[99] Oh, J. I., Urase, T., Kitawaki, H., Rahman, M. M., Rahman, M. H. & Yamamoto, K. (2000). Modeling of arsenic rejection considering affinity and steric hindrance effect in nanofiltration membranes. *Water Science & Technology*, *42*, 173-180.
[100] Orange County Water District - Groundwater Authority, (2002) Orange County Water District takes a proactive stance on contaminants of concern, Retrieved March 17, 2009 from http://www.ocwd.com/_html/_pr/_pr02/pr02_0129_dioxane.htm.
[101] Orange County Water District, (2007) OCWD set to build advanced water quality assurance laboratory, Retrieved March 17, 2009 from http://www.ocwd.com/fv-98.aspx.

[102] Piccolo, A. (1994). Interactions between organic pollutants and humic substances in the environment. In N. Senesi and T. M. Miano (Eds.), *Humic substances in the global environment and implications on human health*, (pp. 961-979). Amsterdam: Elsevier.
[103] Plakas, K. V., Karabelas, A. J., Wintgens, T. & Melin, T. (2006). A study of selected herbicides retention by nanofiltration membranes - the role of organic fouling. *Journal of Membrane Science*, *284*, 291-300.
[104] Plumlee, M. H., López-Mesas, M., Heidlberger, A., Ishida, K. P. & Reinhard, M. (2008). N-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC-MS/MS. *Water Research*, *42*, 347-355.
[105] Pronk, W., Biebow, M. & Boller, M. (2006). Electrodialysis for recovering salts from a urine solution containing micropollutants. *Environmental Science & Technology*, *40*, 2414-2420.
[106] Pronk, W., Palmquist, H., Biebow, M. & Boller, M. (2006). Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine. *Water Research*, *40*, 1405-1412.
[107] Pronk, W., Zuleeg, S., Lienert, J., Escher, B. I., Koller, M., Berner, A., Koch, G. & Boller, M. (2007). Pilot experiments with electrodialysis and ozonation for the production of a fertiliser from urine. *Water Science & Technology*, *56*, 219-227.
[108] Rabiet, M., Togola, A., Brissaud, F., Seidel, J.-L., Budzinski, H. & Elbaz-Poulichet, F. (2006). Consequences of treated water recycling as regards pharmaceuticals and drugs in surface and ground waters of a medium-sized mediterranean catchment. *Environmental Science & Technology*, *40*, 5282-5288.
[109] Radjenovic, J., Petrovic, M. & Barcelo, D. (2007). Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. *Analytical And Bioanalytical Chemistry*, *387*, 1365-1377.
[110] Radjenovic, J., Petrovic, M., Ventura, F. & Barceló, D. (2008). Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. *Water Research*, *42*, 3601-3610.
[111] Raff, O. & Wilken, R.-D. (1999). Removal of dissolved uranium by nanofiltration. *Desalination*, *122*, 147-150.
[112] Rosa, M. J. & de Pinho, M. N. (1995). The role of ultrafiltration and nanofiltration on the minimisation of the environmental impact of bleached pulp effluents. *Journal of Membrane Science*, *102*, 155-161.
[113] Safe, S. H. (2000). Endocrine disruptors and human health: is there a problem? An update. *Environmental Health Perspectives*, *108*, 487-493.
[114] Sanli, O. & Asman, G. (2000). Removal of Fe (III) ions from dilute aqueous solutions by alginic acid-enhanced ultrafiltration. *Journal of Applied Polymer Science*, *77*, 1096-1101.
[115] Schäfer, A. I. (2001). *Natural organic matter removal using membranes: principles, performance and cost*. Boca Raton: CRC Press.
[116] Schäfer, A. I., Fane, A. G. & Waite, T. D. (Eds.) (2005). Oxford: Elsevier.
[117] Schäfer, A. I., Mastrup, M. & Jensen, R. L. (2002). Particle interactions and removal of trace contaminants from water and wastewaters. *Desalination*, *147*, 243-250.
[118] Schäfer, A. I., Nghiem, L. D. & Oschmann, N. (2006). Bisphenol A retention in the direct ultrafiltration of greywater. *Journal of Membrane Science*, *283*, 233-243.
[119] Schäfer, A. I., Nghiem, L. D. & Waite, T. D. (2003). Removal of the natural hormone estrone from aqueous solutions using nanofiltration and reverse osmosis. *Environmental Science & Technology*, *37*, 182-188.
[120] Schultz, M. M. & Furlong, E. T. (2008). Trace analysis of antidepressant pharmaceuticals and their select degradates in aquatic matrixes by LC/ESI/MS/MS. *Analytical Chemistry*, *80*, 1756-1762.
[121] Seah, H., Poon, J., Leslie, G. & Law, I. B. (2003). Singapore's NEWater demonstration project - another milestone in indirect potable reuse. *Water*, 43-46.
[122] Seidel, A., Waypa, J. J. & Elimelech, M. (2001). Role of charge (Donnan) exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane. *Environmental Engineering Science*, *18*, 105-113.
[123] Sindicat des Eaux d'Ile de France, (2007) Bilan de la qualité des eaux brutes, produites et distribuées en 2007, Retrieved March 17, 2009 from http://www.sedif.com/le_sedif/iso_album/bilan_qualite_des_eaux_2007.pdf.
[124] Sindicat des Eaux d'Ile de France, (2007) Rapport annuel, Retrieved March 17, 2009 from http://www.sedif.com/le_sedif/iso_album/sedif_rap_annuel_2007.pdf.
[125] Singapore Public Utilities Board, P., (2002) Singapore water reclamation study - expert panel review and findings, Retrieved March 17, 2009 from http://www.pub.gov.sg/newater/AboutNEWater/Documents/review.pdf.
[126] Strathmann, H. (2004). *Ion exchange membrane separation processes*. Amsterdam: Elsevier.
[127] Teng, Z., Yuan Huang, J., Fujita, K. & Takizawa, S. (2001). Manganese removal by hollow fiber micro-filter. Membrane separation for drinking water. *Desalination*, *139*, 411-418.
[128] Ternes, T. A. & Joss, A. (Eds.) (2006). London: IWA.
[129] Tortajada, C. (2006). Water Management in Singapore. *Water Resources Development*, *22*, 227-240.
[130] Turek, M., Dydo, P., Trojanowska, J. & Bandura, B. (2007). Electrodialytic treatment of boron-containing wastewater. *Desalination*, *205*, 185-191.
[131] Tyler, C. R., Jobling, S. & Sumpter, J. P. (1998). Endocrine disruption in wildlife: a critical review of the evidence. *Critical Reviews in Toxicology*, *28*, 319-361.
[132] Uludag, Y., Özbelge, H. Ö. & Yilmaz, L. (1997). Removal of mercury from aqueous solutions via polymer-enhanced ultrafiltration. *Journal of Membrane Science*, *129*, 93-99.

[133] Urkiaga, A., Bolaño, N. & De Las Fuentes, L. (2002). Removal of micropollutants in aqueous streams by organophilic pervaporation. *Desalination*, *149*, 55-60.
[134] Van der Bruggen, B., Milis, R., Vandecasteele, C., Bielen, P., Van San, E. & Huysman, K. (2003). Electrodialysis and nanofiltration of surface water for subsequent use as infiltration water. *Water Research*, *37*, 3867-3874.
[135] Van der Bruggen, B., Schaep, J., Maes, W., Wilms, D. & Vandecasteele, C. (1998). Nanofiltration as a treatment method for the removal of pesticides from groundwaters. *Desalination*, *117*, 139-147.
[136] Van der Bruggen, B., Schaep, J., Wilms, D. & Vandecasteele, C. (1999). Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *Journal of Membrane Science*, *156*, 29-41.
[137] Ventresque, C., Gisclon, V., Bablon, G. & Chagneau, G. (2000). An outstanding feat of modern technology: the Méry-sur-Oise nanofiltration Treatment plant (340,000 m3/d). *Desalination*, *131*, 1-16.
[138] Weber, S., Gallenkemper, M., Melin, T., Dott, W. & Hollender, J. (2004). Efficiency of nanofiltration for the elimination of steroids from water. *Water Science and Technology*, *50*, 9–14.
[139] Weston, D. P., You, J. & Lydy, M. J. (2004). Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environmental Science & Technology*, *38*, 2752-2759.
[140] Wilf, M., Hydranautics, a Nitto Denko Corporation. (1998) Advanced membrane technology for water reclamation, Retrieved 17-03-2009 from http://www.membranes.com/docs/papers/18_watertech.pdf.
[141] Williams, M. E., Hestekin, J. A., Smothers, C. N. & Bhattacharyya, D. (1999). Separation of organic pollutants by reverse osmosis and nanofiltration membranes: mathematical models and experimental verification. *Industrial & Engineering Chemistry Research*, *38*, 3683-3695.
[142] Williams, R. J., Johnson, A. C., Smith, J. J. L. & Kanda, R. (2003). Steroid estrogens profiles along river stretches arising from sewage treatment works discharges. *Environmental Science & Technology*, *37*, 1744-1750.
[143] Wu, Y., Kong, Y., Liu, J., Zhang, J. & Xu, J. (1991). An experimental study on membrane distillation-crystallization for treating waste water in taurine production. *Desalination*, *80*, 235-242.
[144] Xu, P., Drewes, J. E., Bellona, C., Amy, G., Kim, T.-U., Adam, M. & Heberer, T. (2005). Rejection of emerging organic micropollutants in nanofiltration-reverse osmosis membrane applications. *Water Environment Research*, *77*, 40-48.
[145] Xu, P., Drewes, J. E., Kim, T.-U., Bellona, C. & Amy, G. (2006). Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications. *Journal of Membrane Science*, *279*, 165-175.
[146] Yoon, Y., Westerhoff, P., Snyder, S. A. & Wert, E. C. (2006). Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. *Journal of Membrane Science*, *270*, 88-100.
[147] Yoon, Y., Westerhoff, P., Snyder, S. A., Wert, E. C. & Yoon, J. (2007). Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes. *Desalination*, *202*, 16-23.
[148] Yoon, Y., Westerhoff, P., Yoon, J. & Snyder, S. A. (2004). Removal of 17β–estradiol and fluoranthene by nanofiltration and ultrafiltration. *Journal of Environmental Engineering*, *130*, 1460-1467.
[149] Younes, M. (1999). Specific issues in health risk assessment of endocrine disrupting chemicals and international activities. *Chemosphere*, *39*, 1253-1257.
[150] Yuan, W. & Zydney, A. L. (2000). Humic acid fouling during ultrafiltration. *Environmental Science and Technology*, *34*, 5043-5050.
[151] Zhang, Y., Causserand, C., Aimar, P. & Cravedi, J. P. (2006). Removal of bisphenol A by a nanofiltration membrane in view of drinking water production. *Water Research*, *40*, 3793-3799.
[152] Zolotarev, P. P., Ugrozov, V. V., Volkina, I. B. & Nikulin, V. M. (1994). Treatment of waste water for removing heavy metals by membrane distillation. *Journal of Hazardous Materials*, *37*, 77-82.
[153] Zuccato, E., Calamari, D., Natangelo, M. & Fanelli, R. (2000). Presence of therapeutic drugs in the environment. *The Lancet*, *355*, 1789-1790.

Table 1 – Selected xenobiotics chemical properties

[a] [93], [b] [65], [c] [74], [d] [128], [e] [88], [f] [91], [g] [48], [h] [72], [i] [119], [j] [148], [k] [94].

Compound	Molecular Formula	CAS No.	Molecular Structure	Molecular weight (g/mol)	Solubility (mg/L)	pK_a	Log K_{ow}	Dipole moment (Debye)	H acceptor (A)/ donor (D) capacity of the compound[1]
Endocrine Disrupting Chemicals									
Bisphenol A (Endocrine Disruptor)	$C_{15}H_{16}O_2$	80-05-7		228	120 [a,b]	9.28 [c]	3.32 [d]	1 -1.4 [a,b,e]	2 strong D [OH]/2 weak A [π electrons]
Estradiol (Natural Steroidal Hormone)	$C_{18}H_{24}O_2$	50-28-2		272	3.6 -13 [b,f]	10.23 [c]	4.01 [g]	2.2 [h]	2 strong D [OH]/1 weak A [π electrons]
Estrone (Natural Steroidal Hormone)	$C_{18}H_{22}O_2$	53-16-7		270	13 -30 [f,j]	10.34 [c]	3.13 [g]	2.1 [h]	1strong D [OH]/1 strong and 1 weak A [=O, π electrons]
Fluoranthene (Polycyclic Aromatic Hydrocarbon)	$C_{16}H_{10}$	206-44-0		202.3	<1	NA	5.2 [j]	NA	3 weak A [π electrons]
Pharmaceuticals									
Carbamazepine (Antiepileptic)	$C_{15}H_{12}N_2O$	298-46-4		236	17.7 [b,k]	<1 [d]	2.45 [d]	3.2-3.6 [b,k]	1strong D [NH_2]/2 strong and 2 weak A [=O, N, 2 π electrons]
Sulfamethoxazole (Sulfonamide antibiotic)	$C_{10}H_{11}N_3O_3S$	723-46-6		253	600-610 [b,k]	1.8, 5.7 [d,k]	0.89 [b,d,k]	5.4 -6.3 [b,k]	2 strong D [NH, NH_2]/4 strong and 1 weak A [2 =O, N, O, π electrons]

[1] The H acceptor and donor groups of the compound are identified in brackets [group]

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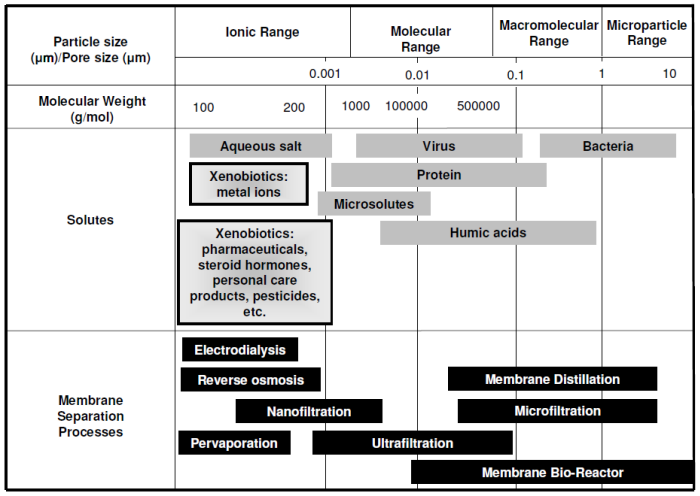
(In) Xenobiotics in the Urban Water Cycle: Mass Flows, Environmental Processes and Mitigation Strategies, Bester, K. ; Kümmerer, K. ; Fatta-Kassinos, D. (Eds)
Springer Environmental Book Series, Environmental Pollution, Vol. 16,
Springer, Hardcover, ISBN: 978-90-481-3508-0, 480 pp.

Table 2 - Membrane processes and contaminants dimensions (adapted from [6, 7, 77, 84, 115])



Figures

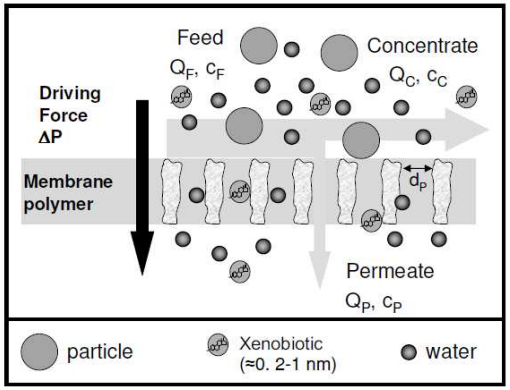


Figure 1 – Pressure-driven membrane schematic with pore size d_p (microfiltration, ultrafiltration, nanofiltration and reverse-osmosis)

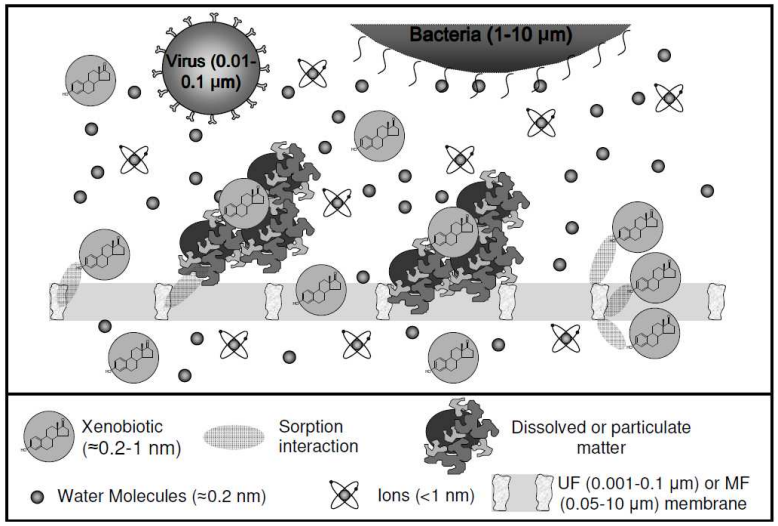


Figure 2 – Retention mechanisms by MF and UF membranes

Semião, A.J.C. ; Schäfer, A.I. (2010) Xenobiotics removal by membrane technology: An overview,
(In) Xenobiotics in the Urban Water Cycle: Mass Flows, Environmental Processes and Mitigation Strategies, Bester, K. ; Kümmerer, K. ; Fatta-Kassinos, D. (Eds)
Springer Environmental Book Series, Environmental Pollution, Vol. 16,
Springer, Hardcover, ISBN: 978-90-481-3508-0, 480 pp.

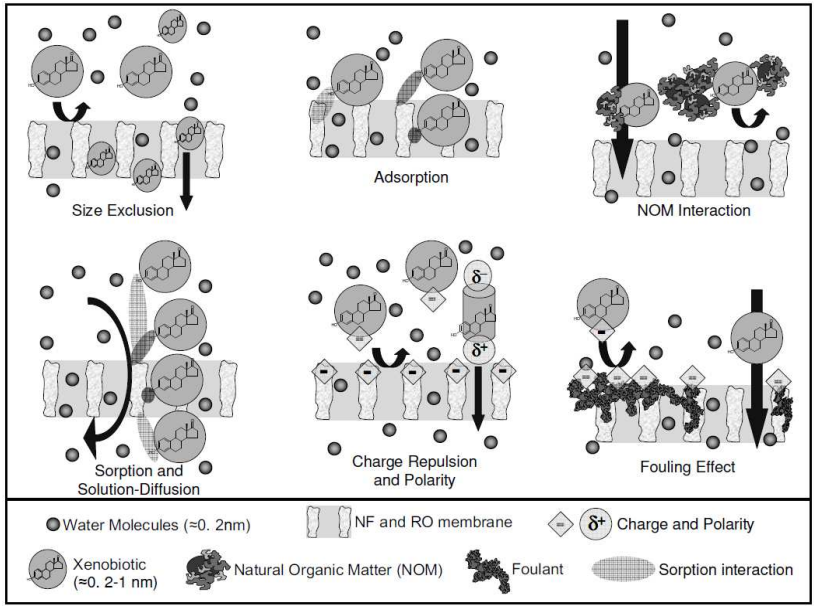


Figure 3 – Retention mechanisms by NF and RO membranes

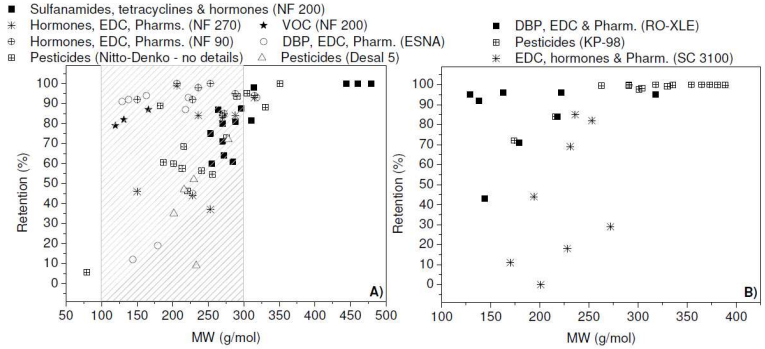


Figure 4 – Xenobiotics retention by NF (A) and RO (B) membranes as a function of MW – the shaded area corresponds to the MWCO of the NF membranes (adapted from [24, 14, 35, 66, 64, 65, 88, 70]) with EDC: Endocrine Disrupting Chemicals, Pharm: Pharmaceuticals, VOC: Volatile Organic Carbon, DBP: Disinfection By-products and the membrane used specified in [ ]

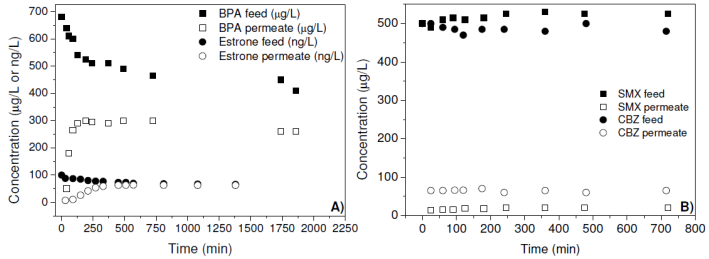


Figure 5 – BPA, estrone (A), SMX and CBZ (B) feed and permeate concentrations progress with time in NF (A and B adapted from [93, 56] and [94] respectively)

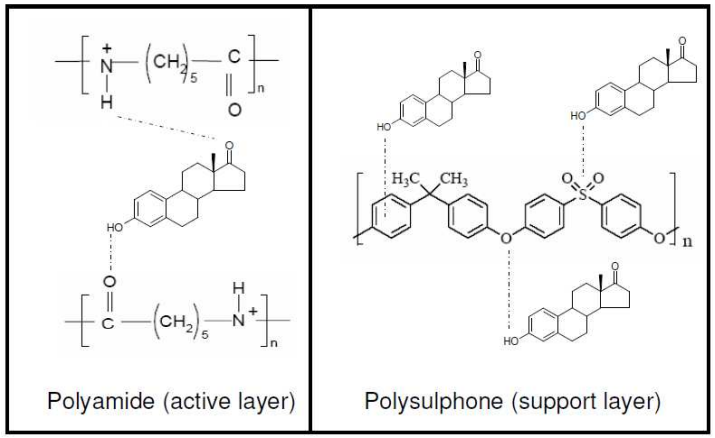


Figure 6 – H-bonding between xenobiotics and polyamide and polysulphone membranes

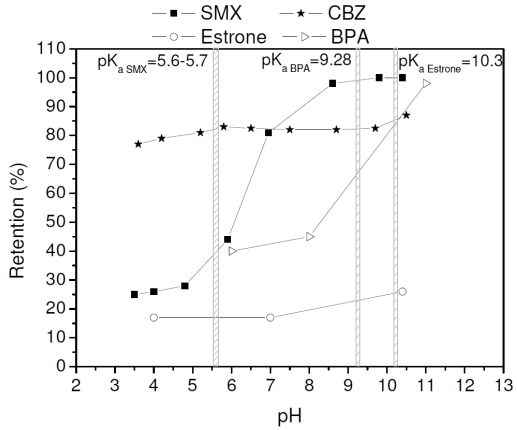


Figure 7 – SMX, estrone, BPA and CBZ retention as a function of pH (adapted from [93, 94, 55, 97])